

REQUEST FOR FILING NATIONAL PATENT APPLICATION

Under 35 USC 111(a) and Rule 53(b)

(Not for Provisional or PCT cases)

PATENT
APPLICATION

WITH SIGNED DECLARATION

NONPROVISIONAL

Asst. Commissioner of Patents
Washington, D.C. 20231

Herewith is the PATENT APPLICATION of
Inventor(s): Tomohiro MAEKAWA

Title LAMINATED EXTRUDED RESIN SHEET

(Our Deposit Account No. 03-3975)

Our Order No. 70104 255979
C# M#

Atty. Dkt.: PMS 255979 555372
M# Client Ref

Date: September 28, 1998

including:

1. Specification: 28 pages (only spec. and claims) 2. ☐ Specification in non-English language
3. Declaration ☒ Original ☐ Facsimile/Copy ☒ Abstract 1 page(s); 8 numbered claims
3 (a). ☒ Drawings: 1 sheet(s) ☐ informal; ☒ formal of size: ☒ A4 ☐ 11" ☐ 13"
4. **AMEND the specification** please by inserting before the first line: — This is a ☐ Continuation-in-Part
☐ Divisional ☐ Continuation ☐ Substitute Application (MPEP 201.09) of:
4(a) ☐ National Appln. No. / filed (M#)
4(b) ☐ International Appln. No. / filed / which
designated the U.S.
5. ☐ See top first page re continuing application ("X" box only if information is there)
6. ☒ Attached is an assignment and cover sheet. Please return the recorded assignment to the undersigned.
7. ☐ Prior application is assigned to

by Assignment recorded / Reel / Frame /

8. **FOREIGN** priority is claimed under 35 USC 119(a)-(d)/365(b) based on filing in JAPAN

Application No.	Filing Date	Application No.	Filing Date
(1) 09-270105	October 2, 1997	(2)	
(3)		(4)	
(5)		(6)	
(7)		(8)	
(9)		(10)	

10. 1 (No.) Certified copy (copies): ☒ attached; ☐ previously filed (date) /
in U.S. Application No. / filed on /

11. ☐ Attached: / (No.) Verified Statement(s) establishing "small entity" status under Rules 9 & 27.

12. **DOMESTIC/INTERNATIONAL** priority is claimed under 35 USC 119(e)/120/365(c) based on the following provisional,
nonprovisional and/or PCT international application(s):

Application No.	Filing Date	Application No.	Filing Date
(1)		(2)	
(3)		(4)	
(5)		(6)	
(7)		(8)	
(9)		(10)	

13. ☒ Attached: Form PTO-1449 copy listed references.

14. ☐ This application is being filed under Rule 53(b)(2) since an inventor is named in the enclosed Declaration who was not named in the prior application.

15. ☐ Preliminary Amendment:

THE FOLLOWING FILING FEE IS BASED ON CLAIMS AS FILED LESS ANY ABOVE CANCELLED

				Large/Small Entity		Fee Code
16. Basic Filing Fee				\$790/\$395	\$790	101/201
17. Total Effective Claims	8	minus 20 =	*0	x \$22/\$11 =	+ 0	103/203
18. Independent Claims	1	minus 3 =	*0	x \$82/\$41 =	+ 0	102/202
*If answer is zero or less, enter "0"						
19. If any proper multiple dependent claim (ignore improper) is present, add (Leave this line blank if this is a reissue application)				+ \$270/\$135	+ 0	104/204
20. TOTAL FILING FEE ENCLOSED =				\$790		
21. If "non-English" box 2 is X'd, add Rule 17(k) processing fee				+ \$130/\$130	+ 0	139
22. If "assignment" box 6 is X'd, add recording fee				+ \$40/\$40	+ 40	581
23. <input type="checkbox"/> Attached is a Petition/Fee under Rule No.				+ \$130/\$130	+ 0	122
24. TOTAL FEE ENCLOSED =				\$830		

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APPLICATION UNDER UNITED STATES PATENT LAWS

Invention: LAMINATED EXTRUDED RESIN SHEET

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This is a:

- ☐ Provisional Application
- ☒ Regular Utility Application
- ☐ Continuing Application
- ☐ PCT National Phase Application
- ☐ Design Application
- ☐ Reissue Application
- ☐ Plant Application
- ☐ Substitute Specification

Sub. Spec Filed _____
in App. No. _____ / _____

SPECIFICATION

TITLE OF THE INVENTION

LAMINATED EXTRUDED RESIN SHEET

BACKGROUND OF THE INVENTION

5 Field of the Invention

The present invention relates to a laminated extruded resin sheet comprising a methyl methacrylate resin, particularly, a laminated extruded resin sheet comprising a methyl methacrylate resin which is subjected to secondary
10 thermoforming to obtain a formed article having smaller bias of thickness.

Description of the Related Art

A methyl methacrylate resin is a resin having excellent transparency and light resistance, and widely used in an
15 optical material, lighting cover, illumination signboard and the like.

This methyl methacrylate resin is also excellent in secondary thermoforming property, and can be endowed with specific form by heating at temperature over heat
20 deformation temperature and draw forming, after extruding once to form a sheet.

Examples of this secondary thermoforming method include free blow forming, free vacuum forming, pushing up forming, ridge forming, straight forming, drape forming,
25 reverse draw forming, air slip forming, plug assist forming,

plug assist reverse draw forming and the like, these forming methods are used alone or in combination to obtain desired form.

Recently, a lighting cover having corner portion
5 extremely extruding and deep bath tub come to produce by super draw forming, and the forms of molded articles come increasingly further complicated by progress in forming technology itself.

High draw forming with short heating time or heating
10 at low temperature also come to carry out as the development of the forming processing technology, therefore, resins to be formed are also required to be designed so as to cope with the severe conditions in this forming.

When the above-mentioned high draw forming is conducted
15 using a conventional methyl methacrylate resin, there is a tendency that a sheet is broken in forming, or difference in thickness between high draw part and low draw part of a sheet remarkably increases even if forming is possible.

For solving these problems, there are disclosed an
20 extruded sheet to which a fine particle having specific branched structures is added, and an extruded sheet obtained by allowing a methyl methacrylate polymer having specific cross-linked structure and a rubber-like polymer to be contained in a methyl methacrylate resin, for example, in
25 Japanese Patent Application Laid-Open (JP-A) No. 9-208,789.

The extruded sheet described in JP-A 9-208789 is excellent, however, since it is liable to be contracted in effecting secondary thermoforming, there is a tendency that a uniform thin sheet is not easily obtained unless cooling
5 condition is successfully controlled in producing an extruded sheet. Therefore, there is a problem that slight difference in forming property occurs between a sheet produced in summer and a sheet produced in winter in an extrusion production factory of which temperature control
10 is difficult. Further, this sheet is expensive since effective ingredients are dispersed in the whole plate.

Then, the present inventors have intensively studied an extruded resin sheet comprising a methyl methacrylate resin which produced without specific conditioning in
15 extrusion molding, and as a result, found that there is obtained a laminated extruded resin sheet comprising a methyl methacrylate resin which is produced without being influenced by cooling condition in producing an extruded sheet and can be subjected to secondary thermoforming to
20 obtain a molded article having smaller bias of thickness, only by laminating thin layers of a methyl methacrylate resin in which a insoluble specific acrylic resin particle is dispersed onto both surfaces of a sheet of a methyl methacrylate resin in which the specific amount of a
25 rubber-like polymer is dispersed, completing the present

invention.

SUMMARY OF THE INVENTION

An object of the present invention is to provide a
5 laminated extruded resin sheet comprising a methyl
methacrylate resin which is produced without being
influenced by cooling condition in producing an extruded
sheet and can be subjected to secondary thermoforming to
obtain a molded article having smaller bias of thickness.

10 That is, the present invention is a laminated extruded
resin sheet comprising a methyl methacrylate resin produced
by laminating resin layers (B) on both surfaces of a resin
layer (A) by a multilayer-extrusion molding method, the
resin layer (A) being made by dispersing uniformly 0 to 50
15 parts by weight of a rubber-like resin into 100 parts by
weight of a methyl methacrylate resin, and the resin layer
(B) being made by dispersing uniformly 1 to 50 parts by weight
of a insoluble methyl methacrylate resin particle having
a weight-average particle size of 0.1 to 100 μ m based on
20 100 parts by weight of a base resin comprising 100 parts
by weight of a methyl methacrylate resin and 0 to 70 parts
by weight of a rubber-like polymer.

BRIEF DESCRIPTION OF THE INVENTION

25 Figure. 1 is an appearance view of the molded article

obtained by forming the laminated extruded resin sheet in the example of the present invention.

The number of 0 to 8 represents measuring points for article thickness.

5

DETAILED DESCRIPTION OF THE INVENTION

The methyl methacrylate resin in the present invention is a resin comprising 50% by weight or more of a methyl methacrylate polymer, and may also be a copolymer comprising 10 50% by weight or more of a methyl methacrylate unit and a monofunctional unsaturated monomer unit as a constituent.

Examples of the monofunctional unsaturated monomer unit which is copolymerizable with methyl methacrylate are methacrylates such as ethyl methacrylate, butyl 15 methacrylate, cyclohexyl methacrylate, phenyl methacrylate, benzyl methacrylate, 2-ethylhexyl methacrylate, 2-hydroxyethyl methacrylate and the like; acrylates such as methyl acrylate, ethyl acrylate, butyl acrylate, cyclohexyl acrylate, phenyl acrylate, benzyl 20 acrylate, 2-ethylhexyl acrylate, 2-hydroxyethyl acrylate and the like; unsaturated acids such as methacrylic acid, acrylic acid and the like; styrene, α -styrene, acrylonitrile, methacrylonitrile, maleic anhydride, phenylmaleimide, cyclohexylmaleimide, and the like.

25 Further, this copolymer may also contain a glutaric

anhydride unit, glutarimide unit.

The rubber-like polymer in the present invention is an acrylic polymer having multilayer structure, or a graft copolymer obtained by graft-polymerizing 5 to 80 parts by weight of a rubber with 95 to 20 parts by weight of an ethylenically unsaturated monomer, particularly an acrylic unsaturated monomer, and the like.

The acrylic polymer having multilayer structure has 20 to 60 parts by weight of a layer of an elastomer as an inner component, and has a hard layer as an outermost layer, and may also further contain a hard layer as an innermost layer.

The layer of an elastomer means a layer of an acrylic polymer which has a glass transition temperature (T_g) of less than 25°C and comprises a polymer obtained by cross-linking at least one monoethylenically unsaturated monomer such as a lower alkyl acrylate, lower alkyl methacrylate, lower alkoxy acrylate, cyanoethyl acrylate, acrylamide, hydroxy lower alkyl acrylate, hydroxy lower alkyl methacrylate, acrylic acid, methacrylic acid with a polyfunctional monomer.

The polyfunctional monomer means a monomer which can be copolymerized with the above-mentioned monoethylenically unsaturated monomers, and excludes conjugated dienes.

Examples of the polyfunctional monomer are alkyldiol di(meth)acrylates such as 1,4-butanediol di(meth)acrylate and neopentyl glycol di(meth)acrylate; alkylene glycol di(meth)acrylates such as ethylene glycol di(meth)acrylate, 5 diethylene glycol di(meth)acrylate, tetraethylene glycol di(meth)acrylate, propylene glycol di(meth)acrylate and tetrapropylene glycol di(meth)acrylate; aromatic polyfunctional compounds such as divinylbenzene and diallyl phthalate; polyhydric alcohol (meth)acrylate of such as 10 trimethylolpropane tri(meth)acrylate and pentaerythritol tetra(meth)acrylate, and allyl methacrylates, and the like.

These monomers may be used in combination of two or more.

The hard layer is a layer of an acrylic polymer which 15 has T_g of 25°C or more, and comprise a polymer of an alkyl methacrylate having an alkyl group having 1 to 4 carbon atoms or a copolymer of this alkyl methacrylate with a copolymerizable monofunctional monomer such as another alkyl methacrylate, alkyl acrylate, styrene, substituted 20 styrene, acrylonitrile, methacrylonitrile and the like. It may also be a cross-linked polymer obtained by further adding a polyfunctional monomer and polymerizing them.

Examples of the acrylic polymer having multilayer structure are those described in Japanese Patent 25 Application Publication (JP-B) No. 55-27,576, JP-A Nos.

6-80,739 and 49-23,292.

Examples of a rubber in the graft copolymer mentioned above are diene rubber such as polybutadiene rubber, acrylonitrile-butadiene copolymer rubber, styrene-
5 butadiene copolymer rubber and the like, acrylic rubber such as polybutyl acrylate, polypropyl acrylate, poly-2-ethylhexyl acrylate and the like, and ethylene-propylene-non-conjugated diene rubber, and the like.

Examples of the ethylenic monomers used for graft-
10 polymerizing this rubber are styrene, acrylonitrile, alkyl (meth)acrylate and the like.

As this graft copolymer, those described in JP-A No. 55-147,514 and JP-B No. 47-9,740 can be used.

The amount of the rubber-like polymer dispersed in the
15 resin layer (A) is from 0 to 50 parts by weight, preferably from 3 to 20 parts by weight based on 100 parts by weight of the methyl methacrylate resin. When this amount is over 50 parts by weight, the Young's modulus in fluxure of a sheet lowers.

20 The amount of the rubber-like polymer dispersed in the resin layer (B) is from 0 to 70 parts by weight, preferably from 5 to 50 parts by weight based on 100 parts by weight of the methyl methacrylate resin. When this amount is over 70 parts by weight, the surface of a sheet plate is softened,
25 and is easily scratched in forming processing.

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The insoluble methyl methacrylate resin particle is a resin particle which is not dissolved into the methyl methacrylate resin in which the above-mentioned resin particle is dispersed, even in extrusion-molding and injection-molding. Example of this insoluble resin particle is a methyl methacrylate resin particle having high molecular weight or a cross-linked methyl methacrylate resin particle.

A resin particle having high molecular weight is obtained by polymerization of methyl methacrylate, or by co-polymerization of 50% by weight or more, preferably 80% by weight or more of methyl methacrylate and a monomer having one radical-polymerizable double bond in the molecule. This resin particle has a weight-average molecular weight (Mw) of 500,000 to 5,000,000.

Examples of the monomer having in the molecule one radical-polymerizable double bond are ethyl methacrylate, butyl methacrylate, cyclohexyl methacrylate, phenyl methacrylate, benzyl methacrylate, 2-ethylhexyl methacrylate, 2-hydroxyethyl methacrylate, methyl acrylate, ethyl acrylate, butyl acrylate, cyclohexyl acrylate, phenyl acrylate, benzyl acrylate, 2-ethylhexyl acrylate, 2-hydroxyethyl acrylate, methacrylic acid, acrylic acid, styrene, chlorostyrene, bromostyrene, vinyltoluene, α -methylstyrene and the like. These

monomers may be used in combination of two or more.

A cross-linked resin particle is obtained by copolymerization of monomers having in the molecule at least two double bonds with methyl methacrylate, or by copolymerization of 50% by weight or more of methyl methacrylate, a monomer having in the molecule one radical-polymerizable double bond and a monomer having in the molecule at least two radical-polymerizable double bonds.

The monomer having in the molecule at least two radical-polymerizable double is copolymerizable with the above-mentioned monomers and excludes conjugated dienes, and the above-mentioned polyfunctional monomers are listed as examples.

This cross-linked resin particle has gel ratio of 10% or more which is measured by dissolving the particle in acetone.

The composition of the insoluble methyl methacrylate resin particle is allowable providing it is within the above-mentioned composition, and preferably, it is as near as possible the composition of the methyl methacrylate resin which is a base resin. Specifically, it is desirable that the difference of a ratio of the methyl methacrylate monomer unit constituting a base resin and a ratio of the methyl methacrylate monomer unit constituting the resin particle

does not exceed 30%. When the difference is over 30%, the bias of thickness of the molded article in effecting secondary thermoforming may sometimes be not lowered.

The insoluble methyl methacrylate resin particle is
5 obtained by polymerizing these constituent components by a method such as an emulsion polymerization method, dispersion polymerization method, suspension polymerization method, micro-suspension polymerization method and the like.

10 The particle size of the insoluble methyl methacrylate resin particle of the present invention is from 0.1 to 100 μ m in terms of weight-average particle size. When it is less than 0.1 μ m, the bias of thickness of the molded article in secondary thermoforming is not lowered, and when
15 over 100 μ m, the impact resistance of a sheet is lowered.

The amount of the insoluble resin particle dispersed into the resin layer (B) is from 1 to 50 parts by weight, preferably from 3 to 20 parts by weight based on 100 parts by weight of a base resin comprising 100 parts by weight
20 of a methyl methacrylate resin and 0 to 70 parts by weight of a rubber-like polymer. When it is less than 1 part by weight, the bias of thickness of the molded article is not lowered even if secondary thermoforming is conducted, and when over 50 parts by weight, the impact resistance of a
25 sheet lowers.

The thickness of the laminated extruded resin sheet in the present invention is not particularly restricted, and preferably from 0.1 to 10 mm.

Regarding constitution of layers, it is necessary that
5 the resin layers (B) cover the both surfaces of the resin layer (A). When only one surface is covered, the bias of thickness of the formed article is not lowered.

The layer thickness ratio [resin layer (B)/resin layer (A)/resin layer (B)] is approximately from 1/200/1 to 1/1/1,
10 and preferably from 1/50/1 to 1/2/1. When the resin layer (B) is too thin, the bias of thickness of the molded article is not lowered, and on the other hand when the resin layer (A) is too thin, the dispersion amount itself of the insoluble particle increases and demerit occurs in cost
15 though the bias of thickness of the molded article is lowered.

For preparing a composition in which the rubber-like polymer and insoluble resin particle are dispersed in the methyl methacrylate resin, public-known methods can be
20 applied. Namely, there is a method in which these components are mechanically mixed by a Henschel mixer, tumbler mixer and the like, and melted and kneaded by a Banbury mixer or single screw or twin screw extruder. Further, it is also possible to make a laminated extruded
25 resin sheet in one step using the multilayer-extrusion

molding method described below.

For making laminated extruded resin sheet from the resulted composition, public-known multilayer-extrusion molding methods are used. The multilayer-extrusion

5 molding method is a method in which compositions of the resin layer (A) and the resin layer (B) are melted and kneaded by two or three single or twin screw extruders, then, the compositions are laminated through a feed block die or multi manifold die, and a laminated melted resin sheet is cooled
10 for solidification using a roll unit to obtain a laminated extruded resin sheet.

In the resin layer (A) and the resin layer (B), additives such as a light diffusing agent, dye, optical stabilizer, ultraviolet absorber, antioxidant, releasing
15 agent, flame retardant, anti-electrostatic agent and the like are dispersed without specific problems in addition to the above-mentioned materials, and of course, they can be dispersed in combination of two or more.

The laminated extruded resin plate comprising a methyl
20 methacrylate resin of the present invention provides a molded article having smaller bias of thickness in secondary thermoforming, and suitably used as materials for a lighting cover, bath tub, various toys and the like on which high drawing and complicated forming is performed.

25

Examples

The following examples further illustrate the present invention, but do not limit the scope thereof.

Extrusion apparatuses used in the examples are as follows.

- Extruder ①: screw diameter 40 mm, single screw, with bent (manufactured by Tanabe Plastics Machinery Co.,Ltd.)

- Extruder ②: screw diameter 20 mm, single screw, with bent (manufactured by Tanabe Plastics Machinery Co.,Ltd.)

- Feed block: two kinds three layer distribution (manufactured by Tanabe Plastics Machinery Co.,Ltd.)

- Die: T die, lip width 250 mm, lip distance 6 mm

- Roll: Three polishing rolls, vertical type

The evaluation methods are as follows.

15 (1) Weight-average particle size

It was measured by a particle size analyzer (micro track particle size analyzer Model 9220 FRA, manufactured by Leeds & Northrup, Ltd.), and D_{50} value was adopted as an average particle size.

20 (2) Confirmation of thickness

The composition of the resin layer (B) was temporarily colored, the end surface of the resulted laminated extruded resin sheet produced by use of this colored composition was observed with a $\times 15$ magnifier and the thickness of the laminated part was confirmed.

(3) Thermoforming

A laminated extruded resin sheet of 30 cm × 20 cm was heated from both sides by far infrared panel heaters so that the surface temperature rose up to 140°C and 170°C, and a
5 molded article as shown in Fig. 1 was obtained by using a pushing up forming machine (TF-300 type manufactured by Osaka Banki Seisakusho Co., Ltd., pushing up area; 10 cm × 5 cm, pushing up height; 10 cm).

(4) Thickness measurement

10 The thicknesses of a formed article at points "0", "1" to "8" shown in Fig. 1 were measured by a ultrasonic thickness measuring machine (ULTRASONIC GAGE MODEL 5222, manufactured by PANAMETRICS Ltd.).

"0" represents the center point of summit, and "1" to
15 "8" represent points which are downwardly extended points by 1 cm respectively from the center summit of the side surface of a molded article.

Reference Example 1

20 [Production of rubber-like polymer]

An acrylic polymer having three-layer structure was produced according to a method described in the example of JP-B No. 55-27,576.

Into a glass reaction vessel having an inner volume
25 of 5 L was charged 1700 g of ion-exchanged water, 0.7 g of

sodium carbonate and 0.3 g of sodium persulfate, and the mixture was stirred under nitrogen flow, and after 4.46 g of an emulsifier (Pellex OT-P , manufactured by Kao Corp.), 150 g of ion-exchanged water, 150 g of methyl methacrylate and 0.3 g of allyl methacrylate were charged, the mixture was heated up to 75°C and stirred for 150 minutes.

Then, to this was added a mixture of 689 g of butyl acrylate, 162 g of styrene and 17 g of allyl methacrylate and a mixture of 0.85 g of sodium persulfate, 7.4 g of an emulsifier (Pellex OT-P, manufactured by Kao Corp.) and 50 g of ion-exchanged water via separate inlets over 90 minutes and the resulted mixture was further polymerized for 90 minutes.

After completing the polymerization, a mixture of 326 g of methyl acrylate and 14 g of ethyl acrylate and 30g of ion-exchanged water into which 0.34 g of sodium persulfate had been dissolved were added via separate inlets over 30 minutes. After completing the addition, the mixture was kept for further 60 minutes to complete the polymerization.

The resulted latex was added into a 0.5% aqueous aluminum chloride solution to flocculate a polymer. This polymer was washed five times with hot water, and dried to obtain an acrylic polymer having three layer structure.

Reference Example 2

[Production of a cross-linked methyl methacrylate resin

particle]

Into a glass reaction vessel having an inner volume of 2 L was charged 1200 g of ion-exchanged water, 0.4 g of sodium polymethacrylate (Mw = 7,000,000 , manufactured by Wako Pure Chemical Co., Ltd.), 1.2 g of polyoxyethylene polyoxypropylene ether (Pluronic F 68, manufactured by Asahi Denka Co.,Ltd.) and 1.2 g of disodium hydrogen phosphate, then, a monomer mixture comprising of 380 g of methyl methacrylate, 17 g of methyl acrylate, 2 g of ethylene glycol dimethacrylate, 0.8 g of lauroyl peroxide and 1.5 g of n-dodecylmercaptan was charged.

With stirring at 800 rpm, 0.4 g of sodium polymethacrylate was continuously added at 75°C for two hours while the polymerization ratio was within the range from 12 to 100%. After the polymerization, the mixture was washed, dehydrated, dried, then, classified by an air classifier (TC-15N, manufactured by Nisshin Engineering Co.,Ltd.) to obtain a particle having a weight-average particle size of 33 μ .

Examples 1 to 3

[Resin layer (A)]

3 parts by weight of calcium carbonate (manufactured by Maruo Calcium Co., Ltd., average particle size 3 μ) was mixed by a Henschel mixer with 100 parts by weight of a mixture obtained by mixing 100 parts by weight of a methyl

methacrylate resin (Sumipex EXA , manufactured by Sumitomo Chemical Co., Ltd.) and the rubber-like polymer produced in Reference Example 1 in amount shown in Table 1, then, the mixture was melt and kneaded by the extruder ① and fed to a feed block.

[Resin layer (B)]

The cross-linked methyl methacrylate resin particle produced in Reference Example 2 was mixed by a Henschel mixer in amount shown in Table 1 with 100 parts by weight of a mixture obtained by mixing the same methyl methacrylate resin as used in the resin layer (A) and the rubber-like polymer produced in Reference Example 1 in amounts shown in Table 1 respectively, then, the mixture was melt and kneaded by the extruder ② and fed to a feed block.

[Laminated extruded resin sheet]

Multilayer-extrusion molding of three-layer constitution of 0.1 mm/1.8 mm/0.1 mm was conducted using the resin layer (A) as an intermediate layer and the resin layers (B) as surface layers at an extrusion resin temperature of 265°C, to produce a laminated extruded resin sheet having a width of 21 cm.

The evaluation results are shown in Table 2.

Example 4

[Resin layer (A)]

3 parts by weight of calcium carbonate (manufactured

by Maruo Calcium Co., Ltd., average particle size 3 μ) was mixed by a Henschel mixer with 100 parts by weight of a mixture obtained by mixing 100 parts by weight of the same methyl methacrylate resin as used in Example 1 and the rubber-like polymer produced in Reference Example 1 in amount shown in Table 1, then, the mixture was melt and kneaded by the extruder ① and fed to a feed block.

[Resin layer (B)]

The cross-linked methyl methacrylate resin particle produced in Reference Example 2 was mixed by a Henschel mixer in amount shown in Table 1 with 100 parts by weight of a mixture obtained by mixing the same methyl methacrylate resin as used in the resin layer (A) and the rubber-like polymer produced in Reference Example 1 in amounts shown in Table 1 respectively, then, the mixture was melt and kneaded by the extruder ② and fed to a feed block.

[Laminated extruded resin sheet]

Multilayer-extrusion molding of three-layer constitution of 0.2 mm/2.6 mm/0.2 mm was conducted using the resin layer (A) as an intermediate layer and the resin layers (B) as surface layers at an extrusion resin temperature of 265°C, to produce a laminated extruded resin sheet having a width of 21 cm.

The evaluation results are shown in Table 2.

Example 5

[Resin layer (A)]

1.6 parts by weight of calcium carbonate (manufactured by Maruo Calcium Co., Ltd., average particle size 3 μ), 0.02 parts by weight of titanium oxide (manufactured by Ishihara Sangyo Co., Ltd.) and 0.5 parts by weight of a sodium alkyl sulfonate (having 15 to 16 carbon atoms, straight chain) were mixed by a Henschel mixer with 100 parts by weight of a mixture obtained by mixing 100 parts by weight of the same methyl methacrylate resin as used in Example 1 and the rubber-like polymer produced in Reference Example 1 in amount shown in Table 1, then, the mixture was melt and kneaded by the extruder ① and fed to a feed block.

[Resin layer (B)]

0.5 parts by weight of the same sodium alkyl sulfonate as used in the resin layer (A) was mixed by a Henschel mixer with 100 parts by weight of a mixture obtained by mixing the same methyl methacrylate resin as used in the resin layer (A) and the rubber-like polymer produced in Reference Example 1 in amounts shown in Table 1 respectively, then, the mixture was melt and kneaded by the extruder ② and fed to a feed block.

[Laminated extruded resin sheet]

Multilayer-extrusion molding of three-layer constitution of 0.2 mm/2.6 mm/0.2 mm was conducted using the resin layer (A) as an intermediate layer and the resin

layers (B) as surface layers at an extrusion resin temperature of 265°C, to produce a laminated extruded resin sheet having a width of 22 cm and a thickness of 3 mm.

The evaluation results are shown in Table 2.

5 Example 6

[Resin layer (A)]

1.6 parts by weight of calcium carbonate (manufactured by Maruo Calcium Co., Ltd., average particle size 3 μ) and 0.02 parts by weight of titanium oxide (manufactured by Ishihara Sangyo Co., Ltd.) were mixed by a Henschel mixer with 100 parts by weight of a mixture obtained by mixing 100 parts by weight of the same methyl methacrylate resin as used in Example 1 and the rubber-like polymer produced in Reference Example 1 in amount shown in Table 1, then, the mixture was melt and kneaded by the extruder ① and fed to a feed block.

[Resin layer (B)]

0.5 parts by weight of a sodium alkyl sulfonate (having 15 to 16 carbon atoms, straight chain) was mixed by a Henschel mixer with 100 parts by weight of a mixture obtained by mixing the same methyl methacrylate resin as used in the resin layer (A), the rubber-like polymer produced in Reference Example 1 and the cross-linked methyl methacrylate resin particle produced in Reference Example 2 in amounts shown in Table 1 respectively, then, the mixture was melt and kneaded by

the extruder ② and fed to a feed block.

[Laminated extruded resin sheet]

Multilayer-extrusion molding of three-layer constitution of 0.1 mm/1.8 mm/0.1 mm was conducted using
5 the resin layer (A) as an intermediate layer and the resin layers (B) as surface layers at an extrusion resin temperature of 265°C, to produce a laminated extruded resin sheet having a width of 21 cm and a thickness of 2 mm.

The evaluation results are shown in Table 2.

10 Comparative Example 1

The same procedure as in Example 4 was conducted except that one flow route of the resin layer (B) was stopped by feed block operation for two-layer extrusion forming in Example 4. A laminated extruded resin sheet having a width
15 of 20 cm was produced in which the resin layer (B)/the resin layer (A) was 0.2 mm/2.8 mm.

The evaluation results are shown in Table 2.

Comparative Example 2

The same procedure as in Example 4 was conducted except
20 that the materials for resin layer (A) and the resin layer (B) were exchanged in Example 4, to produce a laminated extruded resin sheet.

The evaluation results are shown in Table 2.

Comparative Example 3

25 25 parts by weight of the same rubber-like polymer

produced in Reference Example 1 was mixed by a Henschel mixer with 100 parts by weight of the same methyl methacrylate resin as used in Example 1, then, the mixture was melt and kneaded by the extruder ① and a single-layer extruded resin sheet having a width of 20 cm and a thickness of 3 mm was produced at an extrusion resin temperature of 265°C.

The evaluation results are shown in Table 2.

Comparative Example 4

13 parts by weight of the particle produced in Reference Example 2 was mixed by a Henschel mixer with 100 parts by weight of a mixture of 100 parts by weight of the same methyl methacrylate resin as used in Example 1 and 25 parts by weight of the rubber-like polymer produced in Reference Example 1, then, the mixture was melt and kneaded by the extruder ① and a single-layer extruded resin sheet having a width of 20 cm and a thickness of 3 mm was produced at an extrusion resin temperature of 265°C.

The evaluation results are shown in Table 2.

Table 1

	Layer consti- tution	Resin layer (A)		Resin layer (B)		
		Resin		Resin		Particl e
	mm	PMMA (parts)	Rubber- like polymer (parts)	PMMA (parts)	Rubber- like polymer (parts)	Amount of disper- sion (parts)
Example 1	0.1/1.8/0.1	100	10	100	14	9
Example 2	0.1/1.8/0.1	100	14	100	39	7
Example 3	0.1/1.8/0.1	100	14	100	39	11
Example 4	0.2/2.6/0.2	100	25	100	0	13
Example 5	0.2/2.6/0.2	100	0	100	42	5
Example 6	0.1/1.8/0.1	100	4	100	45	11
Comparative example 1	0.2/2.8	100	25	100	0	13

PMMA : methyl methacrylate resin

parts : parts by weight

Table 2

	Molding temperature	Points for measuring article thickness										Maximum difference
		0	1	2	3	4	5	6	7	8		
		mm	mm	mm	mm	mm	mm	mm	mm	mm	mm	
Example	1	140	1.502	1.547	1.288	1.408	1.535	1.671	1.795	1.922	2.002	0.714
	2	140	1.577	1.615	1.286	1.344	1.469	1.625	1.77	1.918	2.047	0.761
	3	140	1.585	1.644	1.329	1.428	1.544	1.689	1.828	1.948	1.991	0.662
	4	170	2.199	1.216	1.13	1.247	1.487	1.584	1.727	1.87	1.903	1.069
	5	170	1.703	1.591	1.054	1.187	1.324	1.433	1.530	1.650	1.740	0.649
	6	170	1.414	0.765	0.651	0.689	0.775	0.888	0.989	1.122	1.223	0.763
Comparative example	1	170	3.055	1.007	0.993	1.122	1.288	1.47	1.613	1.771	1.885	2.048
	2	170	2.719	1.103	1.116	1.214	1.353	1.477	1.629	1.76	1.774	1.616
	3	170	2.959	0.966	1.01	1.129	1.288	1.461	1.62	1.757	1.835	1.993
	4	170	2.272	1.167	1.022	1.155	1.33	1.53	1.725	1.915	2.022	

What is claimed is:

1. A laminated extruded resin sheet comprising a methyl methacrylate resin produced by laminating a resin layers (B) on both surfaces of a resin layer (A) by a
5 multilayer-extrusion molding method, the resin layer (A) being made by dispersing uniformly 0 to 50 parts by weight of a rubber-like polymer into 100 parts by weight of a methyl methacrylate resin, and the resin layer (B) being made by dispersing uniformly 1 to 50 parts by weight of a insoluble
10 methyl methacrylate resin particle having a weight-average particle size of 1 to 100 μ m based on 100 parts by weight of a base resin comprising 100 parts by weight of a methyl methacrylate resin and 0 to 70 parts by weight of a rubber-like polymer.

15 2. The laminated extruded resin sheet comprising a methyl methacrylate resin according to Claim 1, wherein the methyl methacrylate resin is a resin containing 50% by weight or more of a methyl methacrylate polymer or a copolymer comprising 50% by weight or more of methyl
20 methacrylate unit and a monofunctional unsaturated monomer unit as a constituent unit.

3. The laminated extruded resin sheet comprising a methyl methacrylate resin according to Claim 1, wherein the rubber-like polymer is an acrylic polymer having multilayer
25 structure or a graft copolymer obtained by graft-

polymerizing 5 to 80 parts by weight of a rubber with 95 to 20 parts by weight of an ethylenically unsaturated monomer.

4. The laminated extruded resin sheet comprising a methyl methacrylate resin according to Claim 1, wherein the insoluble methyl methacrylate resin particle is a methyl methacrylate resin particle having high molecular weight or a cross-linked methyl methacrylate resin particle.

5. The laminated extruded resin sheet comprising a methyl methacrylate resin according to Claim 1, wherein the difference of a ratio of the methyl methacrylate monomer unit constituting a base resin and a ratio of the methyl methacrylate monomer unit constituting the resin particle does not exceed 30%.

6. The laminated extruded resin sheet comprising a methyl methacrylate resin according to Claim 1, wherein the amount of the rubber-like polymer dispersed in the resin layer (A) is from 3 to 20 parts by weight.

7. The laminated extruded resin sheet comprising a methyl methacrylate resin according to Claim 1, wherein the amount of the rubber-like polymer dispersed in the resin layer (B) is from 5 to 50 parts by weight.

8. The laminated extruded resin sheet comprising a methyl methacrylate resin according to Claim 1, wherein the layer thickness ratio [resin layer (B)/resin layer

(A)/resin layer (B)] is from 1/200/1 to 1/1/1.

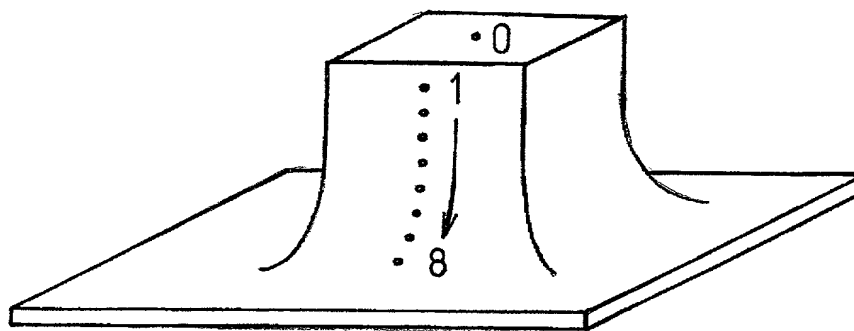
ABSTRACT OF THE DISCLOSURE

5 The present invention provides a laminated extruded resin sheet comprising a methyl methacrylate resin produced by laminating a resin layers (B) on both surfaces of a resin layer (A) by a multilayer-extrusion molding method, the resin layer (A) being made by dispersing uniformly 0 to 50 parts by weight of a rubber-like polymer into 100 parts by weight of a methyl methacrylate resin, and the resin layer (B) being made by dispersing uniformly 1 to 50 parts by weight of a insoluble methyl methacrylate resin particle having a weight-average particle size of 1 to 100 μ m based on 100 parts by weight of a base resin comprising 100 parts by weight of a methyl methacrylate resin and 0 to 70 parts by weight of a rubber-like polymer.

15 The laminated extruded resin sheet comprising a methyl methacrylate resin of the present invention provides a molded article having smaller bias of thickness in secondary thermoforming, and suitably used as materials for a lighting cover, bath tub, various toys and the like on which high drawing and complicated forming is performed.

20

Figure 1



FOR UTILITY/DESIGN
CIP/PCT NATIONAL/PLANT
ORIGINAL/SUBSTITUTE/SUPPLEMENTAL
DECLARATIONS

RULE 63 (37 C.F.R. 1.63)
DECLARATION AND POWER OF ATTORNEY
FOR PATENT APPLICATION
IN THE UNITED STATES PATENT AND TRADEMARK OFFICE

PM&S
FORM

As a below named inventor, I hereby declare that my residence, post office address and citizenship are as stated below next to my name, and I believe I am the original, first and sole inventor (if only one name is listed below) or an original, first and joint inventor (if plural names are listed below) of the subject matter which is claimed and for which a patent is sought on the INVENTION ENTITLED

LAMINATED EXTRUDED RESIN SHEET

the specification of which (CHECK applicable BOX(ES))

X -> [X] is attached hereto.

BOX(ES) -> [] was filed on _____ as U.S. Application No. 0 / _____

-> [] was filed as PCT International Application No. PCT/ _____ / _____ on _____

-> -> and (if U.S. or PCT application amended) was amended on _____

I hereby state that I have reviewed and understand the contents of the above identified specification, including the claims, as amended by any amendment referred to above. I acknowledge the duty to disclose all information known to me to be material to patentability as defined in 37 C.F.R. 1.56. I hereby claim foreign priority benefits under 35 U.S.C. 119/365 of any foreign application(s) for patent or inventor's certificate listed below and have also identified below any foreign application for patent or inventor's certificate filed by me or my assignee disclosing the subject matter claimed in this application and having a filing date (1) before that of the application on which priority is claimed, or (2) if no priority claimed, before the filing date of this application:

PRIOR FOREIGN APPLICATION(S)

Number	Country	Day/MONTH/Year Filed	Date first Laid- open or Published	Date Patented or Granted	Priority Claimed Yes No
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09-270105	Japan	2 October, 1997			X
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I hereby claim domestic priority benefit under 35 U.S.C. 119/120/365 of the indicated United States applications listed below and PCT international applications listed above or below and, if this is a continuation-in-part (CIP) application, insofar as the subject matter disclosed and claimed in this application is in addition to that disclosed in such prior applications, I acknowledge the duty to disclose all information known to me to be material to patentability as defined in 37 C.F.R. 1.56 which became available between the filing date of each such prior application and the national or PCT international filing date of this application:

PRIOR U.S. PROVISIONAL, NONPROVISIONAL AND/OR PCT APPLICATION(S)

Application No. (series code/serial no.)	Day/MONTH/Year Filed	Status pending, abandoned, patented	Priority Claimed Yes No
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I hereby declare that all statements made herein of my own knowledge are true and that all statements made on information and belief are believed to be true; and further that these statements were made with the knowledge that willful false statements and the like so made are punishable by fine or imprisonment, or both, under Section 1001 of Title 18 of the United States Code and that such willful false statements may jeopardize the validity of the application or any patent issued thereon.

And I hereby appoint Pillsbury Madison & Sutro LLP, Intellectual Property Group, 1100 New York Avenue, N.W., Ninth Floor, East Tower, Washington, D.C. 20005-3918, telephone number (202) 861-3000 (to whom all communications are to be directed), and the below-named persons (of the same address) individually and collectively my attorneys to prosecute this application and to transact all business in the Patent and Trademark Office connected therewith and with the resulting patent, and I hereby authorize them to delete names/numbers below of persons no longer with their firm and to act and rely on instructions from and communicate directly with the person/assignee/attorney/firm/ organization who/which first sends/sent this case to them and by whom/which I hereby declare that I have consented after full disclosure to be represented unless/until I instruct the above Firm and/or a below attorney in writing to the contrary.

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(FOR ADDITIONAL INVENTORS, check box [] and attach sheet (PAT-116.2) for same information for each re signature, name, date, citizenship, residence and address.)